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An Ab Initio Study of TiC: A Comparison of Different Levels of Theory Including Density Functional Methods

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Abstract

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An *ab initio* study of TiC: A comparison of different levels of theory including density functional methods

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A comparison is made of various *ab initio* methods, including density functional methods for the $^3\Sigma^+$ and $^1\Sigma^+$ states of TiC. The calculated properties are sensitive to the level of theory. The results with the LSDA and BPW91 density functional methods are in poor agreement with higher level calculations obtained at the MRCI level of theory, but there is better agreement with the B3LYP method. The calculations confirm that the ground state of TiC is the $^3\Sigma^+$ state. © *1996 American Institute of Physics.* [S0021-9606(96)02016-9]

I. INTRODUCTION

The discovery of the met-car compounds M_mC_n by Castleman *et al.*[1] has led to a number of quantum chemical calculations on Ti_8C_{12} and related species. The majority of these calculations used the Hartree–Fock or density functional theory methods. The reliability of these methods for this class of compounds has not been well established. In order to hopefully, establish the reliability of some of these methods, we present here the results of a systematic study on the $^3\Sigma^+$ and $^1\Sigma^+$ states of the simplest Ti–C compound, the diatomic TiC molecule. We propose to continue this study, working up to larger species via TiC_2 and Ti_2C and similar Ti–C species.

The only calculations not using density functional approaches is the CASSCF study of Bauschlicher and Siegbahn.[2] They found the ground state to be the $7\sigma^2 3\pi^4 8\sigma 9\sigma\ ^3\Sigma^+$ state with a $^1\Sigma^+$ state 0.053 eV above it. From their CASSCF calculations on the $^3\Sigma^+$ state they obtained values of 1.76 Å for r_e, 860 cm^{-1} for ω_e, and 3.1 eV for D_e (which they felt to be slightly too small). The $^1\Sigma^+$ state was found to be best described by a combination of the two configurations, $7\sigma^2 3\pi^4 8\sigma^2$ and $7\sigma^2 3\pi^4 9\sigma^2$. The 7σ orbital had mostly C 2s character. The open shell 8σ orbital had Ti 4s and 4p character while the 9σ had C 2p and Ti 3d character. The 3π orbital had Ti 3d and C 2p character.

II. COMPUTATIONAL DETAILS

The titanium basis set was a (14s,11p,6d)/[10s,8p,3d] formed from Wachter's (14s,9p,5d) basis set[3] with the addition of Hay's diffuse 3d function[4] and Hood *et al.*'s 4p functions.[5] For carbon the standard DZP (9s,5p,1d)/[4s,2p,1d] basis set[6,7] was used. This is slightly larger than the (12s8p4d1f)/[5s4p3d1f] basis set used by Bauschlicher and Siegbahn,[2] but without an *f* orbital. It was chosen to allow its use for slightly bigger systems. Some calculations were performed with an extended basis set comprising an *f* function on the Ti atom (α=0.55) and two d functions on the C atom (α=0.35, 1.50, replacing α=0.75). The calculations were performed using the following programs: MOLPRO 94 (Ref. 8) (for some of the HF and CCSD, and all the CASSCF and MRCI calculations), GAUSSIAN 95 (Ref. 9) (for some of the HF and all the DFT calculations), and PSI (Ref. 10) (for some of the CCSD calculations). The CASSCF calculations included the 8 valence electrons with 10 active orbitals formed from the Ti 4s and 3d orbitals and the C 2s and 2p orbitals. The Ti 4p orbitals were not included. The MRCI calculations included all single and double excitations out of any configuration with a CSF whose coefficient was larger than 0.02. The three density functionals used were local spin density approximation (LSDA), Becke's three parameter hybrid method[11] combined with the Lee, Yang, and Parr correlation functional[12] (B3LYP), and Becke's 1988 exchange functional[13] combined with Perdew and Wang's 1991 gradient corrected correlation functional[14] (BPW91).

III. RESULTS AND DISCUSSION

The highest level of theory we have used is the multireference configuration interaction (MRCI) method. In comparing the various methods, we will use it as an approximation to the exact result. The Hartree–Fock based methods we have examined are the restricted open-shell Hartree–Fock (ROHF) method, the complete active space self-consistent field (CASSCF), MRCI, and two coupled cluster approximations, CCSD,[15] and CCSD(T) (Ref. 16) where triple excitations are included. The three density functional approximations were the LSDA, B3LYP and BPW91 methods. The calculated total energies and the singlet–triplet energy differences are given in Table I.

The ground state of Ti is the $3d^2 4s^2\ ^3F$ state. However in bonding the valence state configuration is more likely to be the $3d^3 4s\ ^5F$ state which is observed[17] to lie 0.81 eV above the ground state configuration. The calculated energy differences between these two states are listed in Table I. The various methods vary markedly in their success in calculating the energy difference. The ROHF result is fortuitously close to the experimental result, while two of the

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TABLE I. Total energies of the $^3\Sigma^+$ and $^1\Sigma^+$ States of TiC, TiC singlet–triplet and Ti ^{5}F–^{3}F energy differences.

Method	TiC $^3\Sigma^+$ /hartree	TiC $^1\Sigma^+$ /hartree	$\Delta E(^3\Sigma^+ - ^1\Sigma^+)$ /eV	$\Delta E(^5$F-^{3}F) /eV
ROHF	−886.029 59	−886.007 84	−0.602	0.800
CASSCF	−886.213 16	−886.211 15	−0.055	1.433
MRCI	−886.297 00	−886.291 29	−0.155	1.106
CCSD	−886.477 83	⋯	⋯	1.341
CCSD(T)	−886.508 05	⋯	⋯	1.353
LSDA	−885.538 50	−885.547 34	+0.241	−0.225
B3LYP	−887.359 74	−887.357 25	−0.067	0.226
BPW91	−887.420 00	−887.422 36	+0.067	−0.308
Expt[a]				0.806

[a]Ref. 17.

DFT methods give the incorrect order of the two states. None of the DFT methods are within 0.5 eV of the experimental result. The addition of an *f* function to the Ti basis set does not change this result. Raising the level of theory seems to increase the ^{5}F–^{3}F energy difference, but the MRCI value is less than the CASSCF value.

The LSDA and BPW91 DFT methods also predict the singlet, not the triplet to be the ground state of TiC. The CASSCF singlet–triplet difference is in good agreement with Bauschlicher and Siegbahn's value of 0.053 eV for T_e. With the extended basis set, the difference is slightly closer. For the CASSCF method, the difference is 1.428 eV, and for the MRCI method, it is 1.044 eV. The MRCI calculation increases slightly the triplet–singlet energy difference, confirming that the triplet is the ground state. With the extended basis set the energy difference remains at 0.155 eV.[18] Including 4p orbitals in the CASSCF and MRCI calculations decreased the gap to 0.113 eV.[19] Employing the coupled cluster method, convergence could not be obtained for the closed-shell $^1\Sigma^+$ state when r(Ti–C) >3.2 a_0 even when using sophisticated extrapolation techniques such as the DIIS method.[20] Our CASSCF calculations revealed that the $^1\Sigma^+$ state is not well described by a single determinantal wave function, but has almost equal weights from both the $7\sigma^2 3\pi^4 8\sigma^2$ (0.77), and the $7\sigma^2 3\pi^4 9\sigma^2$ (0.42) configurations. The weight of the $7\sigma^2 3\pi^4 8\sigma 9\sigma$ configuration in the triplet CASSCF calculation is 0.92. Further evidence of the multireference character is provided by the huge τ_1 diagnostic[21] of 0.094 and 0.165 at r(Ti–C)=3.1 and 3.2 a_0, respectively. The 0.165 τ_1 diagnostic is the largest reported to date for a converged calculation. It is usually assumed that τ_1 diagnostics larger than ~ 0.03 are indicative of wave functions with important multireference contributions. The CCSD method predicts that r_e for the $^1\Sigma^+$ state is larger than 3.2 a_0 (1.69 Å). Unfortunately the nonlinear CCSD algebraic equations could not be converged beyond this distance.

TABLE II. Calculated properties of TiC $^3\Sigma^+$ state.

Method	r_e /Å	D_e /eV	ω /cm^{-1}	I.P. /eV	E.A. /eV	μ /D
ROHF	1.617	−1.24	1088	6.11	−3.18	2.90
CASSCF	1.723	2.35	702[a]	5.48	0.21	2.39
MRCI	1.733	2.82	704[a]	6.12	0.52	2.73
CCSD	1.682	2.40	768[a]	6.39	0.58	⋯
CCSD(T)	1.703	3.05	805[a]	6.50	0.65	⋯
LSDA	1.657	6.06	997	7.21	1.90	3.03
B3LYP	1.668	3.60	988	6.70	1.10	3.16
BPW91	1.679	4.79	972	6.56	1.18	3.02

[a]Estimated by curve fitting of energies.

For the $^3\Sigma^+$ state the Mulliken charge on the Ti atom in the ROHF calculations was +0.389. The 3*d* orbital population was 2.429 indicating that for Ti^0 structures the Ti atom is in a $3d^3 4s$ valence state. For the $^1\Sigma^+$ state the Mulliken charge on the Ti atom is +0.327 and the 3*d* population is 2.248.

Selected calculated properties of the $^3\Sigma^+$ state are given in Table II and of the $^1\Sigma^+$ state in Table III. Open shell Hartree–Fock calculations give a much shorter Ti–C bond than that obtained by methods including correlation. At the ROHF level of theory TiC is not bound. This is also reflected in the much larger value of ω_e obtained. With the Hartree–Fock based methods, the inclusion of correlation increases the optimum Ti–C bond length, the higher the level of theory, the larger the increase. The LSDA and BPW91 density functional methods overestimate the dissociation energy D_e. This is undoubtably related to the poor values obtained using these methods for the Ti ^{5}F–^{3}F energy difference. Our calculations suggest that the dissociation energy obtained by Bauschlicher and Siegbahn is not too small, but if anything, slightly high. A similar trend is observed for the harmonic vibrational frequencies ω_e. The density functional methods give larger values for ω_e, especially for the $^1\Sigma^+$ state. Our harmonic vibrational frequencies at higher levels of theory are much smaller than the values of 860 cm^{-1} for the $^3\Sigma^+$ and 700 cm^{-1} for the $^1\Sigma^+$ state obtained by Bauschlicher and Siegbahn.[2] We believe the harmonic vibrational frequencies calculated at the higher levels of theory [CCSD(T) and

TABLE III. Calculated properties of TiC $^1\Sigma^+$ state.

Method	r_e /Å	D_e /eV	ω /cm^{-1}	μ /D
ROHF	1.539	−1.83	1242	7.91
CASSCF	1.784	2.29	579[a]	1.74
MRCI	1.790	2.66	592[a]	2.16
LSDA	1.602	6.30	994	6.41
B3LYP	1.604	3.74	980	6.63
BPW91	1.641	4.85	924	5.79

[a]Estimated by curve fitting of energies.

MRCI] are likely to be closest to the experimental value. While in other respects the B3LYP calculations gave reasonable values for other properties reported here, the value of ω_e may be disappointing, but it is in accord with the usual negative correlation between bond length and ω_e, i.e., the longer the bond length, the smaller the frequency. Our dipole moments are larger for the $^3\Sigma^+$ state and smaller for the $^1\Sigma^+$ state than those given by Bauschlicher and Siegbahn. All the density functional methods give larger values for the vertical I.P.'s and E.A.'s than the Hartree–Fock based methods.

IV. CONCLUSIONS

The results of our calculations confirm that the ground state of TiC is the $^3\Sigma^+$ state with the $^1\Sigma^+$ state lying just above it. The calculated properties are very sensitive to the level of theory. For example the Ti–C bond length increase 0.12 Å in going from the ROHF to the MRCI method. For the ground state $^3\Sigma^+$ state we predict $r_e = 1.72 \pm 0.02$ Å, $D_e \sim 3.0$ eV, $\omega_e = 700$–800 cm^{-1} and the I.P. ~ 6.0–6.5 eV. In comparing the MRCI and the B3LYP calculations for the $^3\Sigma^+$ state, in the B3LYP calculations the bond length is short by 0.035 Å, and the value of D_e is 0.55 eV too large. The values of ω_e, I.P., E.A. and μ are also too large. The LSDA and BPW91 density functional methods may give misleading results due to incorrect state selection, but the B3LYP method appears to give reasonable results for most observables.

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